Indian J. Phys. **77B** (6), 681-685 (2003)

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AN INTERNATIONAL JOURNAL IJP B

Viscous losses of non-polar solvent at microwave frequency 9.8 GHz

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Received 6 May 2003, accepted 12 August 2003

Abstract : The dielectric relaxation time and viscosity of two polar molecules *viz* ethyl acetate and n-butyl acetate in the mixture of paraffin oil (PO) and benzene at different concentrations, have been used to measure the viscous losses at microwave frequencies 9.8 GHz. The visco-elastic relaxation of solute molecule has been used to calculate the real part of the viscosity (η'), viscous loss (η''), and corresponding storage modulus(G'), and loss modulus (G'') at microwave frequencies for both the molecules have been investigated The viscosity lost has also been calculated The great difference of total viscosity loss for dipolar relaxation process, is interpreted in terms of damped oscillatory motion of polar molecules in viscous medium and losses due to restoring force acting on polar molecules by surrounding flexible viscous solvent molecules. A hypothetical equation has been proposed to interpret the difference in the total viscosity loss for dipolar rotation It has been observed that the log τ vs log η' and log τ vs log η'' plots deviates from linearity for higher concentration of PO. and benzene but the plots of η' and η'' were found to be linear

Keywords Dielectric relaxation, viscosity, viscous loss, storage modulus, loss modulus, microwave frequency

PACS Nos. 77.22 Gm, 81.40.Jj, 81.40 Tv, 83 60.Fg

Relaxation phenomenon has been widely used to study the molecular motion in liquids. The microwave absorption studies have been extensively used in understanding the mechanism of dielectric relaxation process when polar molecules in pure liquid state or in dilute solutions of non-polar solvents are subjected to electromagnetic field. Many workers [1-16] studied the dielectric relaxation process involved in polar molecules but the studies of viscosity losses at microwave frequencies are scarce. Earlier workers [4-18] tried to correlate macroscopic observed viscosity (η_0) and dipolar relaxation time (τ) of dipolar molecules. It has been observed by recent observations [11,12,17,19] that log τ *vs* log η_s plots deviate from linearity but the cause of deviation is still not known. Recently, we have calculated the viscous losses at microwave frequencies for some rigid polar molecules namely pyridine, quinoline, bromobenzene and iodobenzene in the solution of benzene and paraffin oil [20]. It is observed that the viscous loss (η'') increases with the increase of concentration of PO in the benzene. In the present study, we shall try to interpret the decrease of $d\tau / d\eta$ slope in terms of viscous losses, present at microwave frequencies. Here, we have taken the ethyl acetate and n-butyl acetate as solute and different concentrations of PO and benzene as solvents will be used to calculate viscous losses at microwave frequencies. The measurement of τ and η of these molecules have been reported earlier by one of us [11].

During the refining of crude oil at high temperature, unsaturated hydrocarbons polymerize and paraffin oil is obtained as the product of petroleum. Therefore, the problem of polar solutes dissolved in highly viscous medium such as paraffin oil and benzene is analogous to polymer solutions because paraffin oil is a typical mineral oil. It is mainly made up of saturated and unsaturated hydrocarbons and not ester / glyceride [21]. Paraffin oil contains naphthanic rings and the paraffin part is present to a large extent in the form of side chain. These aromatic compounds polymerize at higher temperature which is very easily obtained during the petroleum refining process when naphthanic rings come in contact of the air [22-24]. Therefore, the theory of polymers as described in literature [25] can be used to analyze the viscoelastic behavior of P.O. and benzene mixture in highly viscous medium. The polar molecules when relax in highly viscous medium, the simple classification of solid and liquid phase breaks down. The medium is partially solid and partially liquid. The stress employed is proportional to both the

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strain and the rate of strain. Such a medium may be taken to interpret the viscoelastic properties of solid and liquid phase. 'Maxwell Element', can represent the behaviour of viscoelastic medium. as described in literature [25]. The models consist of a spring S and dash pot D showing classical viscous behavior. X_1 represents the extension of spring ($X_1 = T/G_0$ where T is the tension and G_0 is elastic constant). X_2 represents the displacement of dash pot $dX_2 / dt = T / \eta_0$. where η_0 is viscous constant due to solid-liquid phase present in the viscous medium and the total extension

$$X = X_1 + X_2. \tag{1}$$

Suppose at a time $t = 0$, X is suddenly given the value X_0. The immediate effect will be to produce a tension which will cause the dash pot D to move at a rate controlled by tension T and depends on elastic constant (G_0) and viscosity of the solvent (η_0). The motion of 'Maxwell element' is similar to the motion of the polar molecule which relax in viscous medium and depolarization takes place in quasi-solid-liquid phase. Elastic constant (G_0) and observed viscosity (η_0) comes into play to control the motion of 'Maxwell Element' as well as the dielectric relaxation process involved. The equation of motion of the spring is obtained after differentiating the eq. (1) and then integrating, we obtain

$$X_1 = X_0 \exp(-G_0 t / \eta_0). \tag{2}$$

Multiplying both sides by (G_0) and substituting the value of $G_0 X_1 = T$, we get

$$T = G_0 X_0 \exp(-G_0 t / \eta_0). \tag{3}$$

This shows that tension in the spring falls to zero with characteristic relaxation time (τ) of polar molecules ($\tau = \eta_0 / G_0$). Now, suppose an alternating electromagnetic field is applied which varies sinusoidally with time

$X = X_0 \exp(j\omega t)$. In steady state, $X_1 = T/G_0$ and $X_2 = T/j\omega\eta_0$, substituting the value of X_1 and X_2 in eq. (1), it becomes

$$X = T(1/G_0 + 1/j\omega\eta_0). \tag{4}$$

The whole system can be analysed with the help of a complex elastic constant (G^*) and complex viscosity (η^*) at microwave frequencies

$$1/G^* = 1/G_0 + 1/j\omega\eta_0 \tag{5}$$

and $$1/\eta^* = j\omega/G_0 + 1/\eta_0. \tag{6}$$

In term of relaxation time (τ) equation (5) and (6) can be written as

$$G^* = G' + jG'' = G_0 j\omega\tau / 1 + j\omega\tau \tag{7}$$

and $$\eta^* = \eta' - j\eta'' = \eta_0 / 1 + j\omega\tau, \tag{8}$$

where η' is the real part of viscosity and η'' the loss of viscosity, η_0 is the observed viscosity of P.O. Such type of viscoelastic relaxation behavior is also observed in polymers and complex viscosity (η^*) is interpreted in terms of η' and η'' [26-28].

Multiplying the conjugate of eq. (8) and separating it into real and imaginary parts

$$\eta' = \eta_0 / 1 + (\omega\tau)^2 \tag{9}$$

and $$\eta'' = \eta_0 \omega\tau / 1 + (\omega\tau)^2. \tag{10}$$

But eq. (9) is the Barlow and Lamb [8] relation (1959). Above equations are also valid for polymers and derived but Guillermo *et al* using Green-Kubo formula [26-28].

Similarly the complex modulus of rigidity G^* can be separated into real and imaginary parts

$$G' = G_0 \omega\tau / 1 + (\omega\tau)^2 \tag{11}$$

and $$G'' = G_0 \omega^2\tau^2 / 1 + (\omega\tau)^2, \tag{12}$$

where $G_0 = \eta_0 / \tau$. At microwave frequency, the viscosity becomes a complex quantity represented by $\eta^* = \eta' - j\eta''$, where η' is the real part of viscosity or dynamic part of viscosity as suggested by Barlow and Lamb [8]. It plays an important role in the dipolar rotation and follows Debye equation. η'' is the viscous losses of the medium and the resultant viscosity η_M at microwave frequencies is given by

$$\eta_M = \sqrt{\eta'^2 + \eta''^2}. \tag{13}$$

The total viscous loss is

$$\eta_L = \eta_0 - \eta_M, \tag{14}$$

where η_M is the resultant viscosity at microwave frequencies, η_0 is experimental observed viscosity and η_L is the actual viscosity loss. The total viscous loss (η'_L) for dipolar rotation in polar solvent, which follows Debye equation, is calculated by the following equation

$$\eta'_L = \eta_0 - \eta_D, \tag{15}$$

where η_D is the dynamic viscosity as reported earlier [11]. We interpret the difference in the viscosity loss from eqs. (14) and (15) by proposing a new equation for polar molecules which executes damped oscillatory motion in the viscous medium of P.O. and benzene mixture.

$$\eta_M + b\, d\tau / d\eta + v\tau = \eta_0$$

or $$b\, d\tau / d\eta + v\tau = \eta_0 - \eta_M$$

or $$b\, d\tau / d\eta + v\tau = \eta_L, \tag{16}$$

where $b\, d\tau / d\eta$ is the damping force, $v\tau$ is the restoring force, b is a parameter, τ is the dielectric relaxation time and, v is the restoring force per unit relaxation time which depends upon molecules of rigidity (G).

The dielectric relaxation time (τ) is calculated by Higasi *et al*'s method for ethyl acetate and n-butyl acetate as described earlier [11]. The observed viscosity (η_0) for different concentrations of paraffin oil is measured by viscometer. The viscosity (η') and viscous loss (η'') calculated from eqs. (9) and (10) together with viscosity at microwave frequencies (η_M), viscosity loss (η_L), dynamic viscosity (η_D) and total viscosity loss (η'_L) are shown in Table 1. Similarly, storage modulus (G') and loss modulus (G'') for different concentration of P.O. and benzene together with G_M and elasticity modulus losses G_L, G'_L at microwave frequencies are reported in Table 2. These results are also consistent with the studies on polar polymers [29, 30].

It has been assumed that the system follows the limiting case of single viscoelastic relaxation time (τ) in highly viscous medium and viscoelastic relaxation time of solvent is the same as that of the solute. The calculated values of viscosity (η') are 20.74–0.60 (mp), 20.40-0.63 (mp) and viscous loss (η'') are 7.28-0.10 (mp), 8.92–0.11 (mp) of ethyl acetate and n-butyl acetate. The resultant microwave viscosity (η_M) calculated from eq. (13) and values are 21.52–0.61 (mp) and 22.26—0.63 (mp) and viscosity loss (η_L) is calculated from eq. (14) are 1.78–0.01 (mp) and 2.04–0.02 (mp) and total viscosity loss (η'_L) for dipolar rotation which faollows Debye equation, is calculated from eq. (15) and are 19.46–1.39 (mp), 18.57–0.30 (mp) for ethyl acetate and n-butyl acetate at different concentrations of P.O. and benzene mixture. They are reported in Table 1. It is observed from this table that the real part of the viscosity (η') and viscous

Table 1. Relaxation time, observed viscosity, viscosity at microwave frequencies, viscous losses in different dilution of P.O. and benzene.

Polar absorber	Concentration	τ (PS)	η_0 (mp)	η' (mp)	η'' (mp)	η_M (mp)	η_L (mp)	η'_L (mp)	η_D (mp) Literature value[11]
Ethyl Acetate	100% PO	5.7	23.30	20.74	7.28	21.52	1.78	19.46	3.84
	90%P.O. + 10%B[1]	5.4	7.00	6.30	2.09	6.64	0.36	4.70	2.30
	80%PO + 20%B	5.3	3.80	3.43	1.12	3.61	0.16	1.67	2.13
	70%P.O + 30%B	5.1	2.40	2.18	0.69	2.28	0.12	1.39	1.01
	100%B	2.7	0.62	0.60	0.10	0.61	0.01	---	---
n-butyl Acetate	100% PO	7.1	24.30	20.40	8.92	22.26	2.04	18.57	5.73
	90%PO. + 10%B	6.8	9.00	7.66	3.21	8.31	0.69	4.30	4.70
	80%P.O. + 20%B	6.6	5.90	5.06	2.06	5.45	0.45	2.40	3.50
	70%P.O. + 30%B	6.1	2.50	2.19	0.82	2.34	0.16	0.30	2.20
	100%B	2.8	0.65	0.63	0.11	0.63	0.02	---	---

Table 2. Modulus of rigidity and rigidity losses at microwave frequencies in dilution of P.O. and benzene.

Polar Absorber	Concentration	$G_0\times10^{10}$ Dyne/cm^2	$G'\times10^{10}$ Dyne/cm^2	$G''\times10^{10}$ Dyne/cm^2	$G_M\times10^{10}$ Dyne/cm^2	$G_L\times10^{10}$ Dyne/cm^2	$G'_L\times10^{10}$ Dyne/cm^2	$G'_\infty\times10^{10}$ Dyne/cm^2	$G''_\infty\times10^{10}$ Dyne/cm^2	$G''_L\times10^{10}$ Dyne/cm^2
Ethyl Acetate	100% P.O.	4.09	1.28	0.45	1.31	2.78	3.74	0.35	0.18	3.91
	90%P.O + 10%B	1.30	0.34	0.13	0.36	0.94	1.10	0.20	0.08	1.22
	80%P.O + 20%B	0.72	0.21	0.07	0.22	0.50	0.56	0.16	0.06	0.66
	70%P.O. + 30%B	0.47	0.07	0.04	0.08	0.39	0.32	0.15	0.03	0.44
	100%B	0.22	0.03	0.01	0.03	0.19	---	---	---	---
n butyl Acetate	100% P.O.	3.42	1.26	0.55	1.37	2.05	3.06	0.36	0.23	3.19
	90%P.O. + 10%B	1.32	0.47	0.20	0.51	0.81	1.09	0.23	0.13	1.19
	80%P.O. + 20%B	0.89	0.31	0.13	0.34	0.55	0.69	0.20	0.09	0.80
	70%P.O. + 30%B	0.40	0.13	0.05	0.13	0.27	0.24	0.16	0.05	0.35
	100%B	0.23	0.03	0.01	0.03	0.20	---	---	---	---

[1] B-Benzene.

loss (η''),resultant microwave viscosity (η_M) are decreasing with dilution of P.O and benzene mixture. The viscosity loss at microwave frequencies (η_L) and total viscosity loss (η'_L) are also decreasing from P.O to benzene. The total viscosity loss (η'_L) is much larger for pure paraffin oil for both the polar solutes investigated. These results are consistent with our earlier studies on pyridine, quinoline, bromo-benzene and iodo-benzene in the mixture of P.O and benzene [20].

Similarly, the values of storage modulus (G') are 1.28–0.03 dyne/cm^2,1.26–0.03 dyne/cm^2, loss modulus(G'') are 0.45–0.01 dyne/cm^2, 0.55–0.01 dyne/cm^2, resultant microwave modulus of rigidity (G_M) are 1.31–0.03 dyne/cm^2 ,1.37–0.03 dyne/cm^2, modulus of rigidity loss (G_L) are 2.78–0.19 dyne/cm^2, 2.05–0.20 dyne/cm^2 and total modulus of rigidity loss (G_L') are 3.74–0.32 dyne/cm^2, 3.06–0.24 dyne/cm^2 calculated by using extrapolation method and values of (G_L'') are 3.91–0.44 dyne/cm^2, 3.19–0.35 dyne/cm^2 as calculated by using modified equations of ethyl acetate and n-butyl acetate for different concentration of P.O and benzene mixture. They are reported in Table 2. It has been observed from Table 2 that storage modulus (G'), loss modulus (G''), and resultant microwave modulus of rigidity (G_M) are decreasing with the dilution of P.O and benzene mixture. The modulus of rigidity loss (G_L) at microwave frequencies and total modulus of rigidity loss (G_L'), (G_L'') are also decreasing from P.O to benzene. The modulus of rigidity (G_∞) values for these compounds earlier [11] is also decreasing with dilution of P.O and benzene. There are considerable differences in the calculated values of total viscosity loss (η_L), (η'_L) and modulus of rigidity loss (G_L), (G_L'), and (G_L''). It means that some other viscous losses are present at microwave frequencies. Therefore, we propose equation (16) to explain the discrepancy in viscosity at microwave frequencies. The polar molecules execute damped oscillatory motion in viscous medium of P.O and benzene.

The rate of increase of relaxation time (τ) is very slow as compared to the increase in the observed static viscosity (η_0) of the solvent. The plots of log τ vs log η' and log τ vs log η'' deviates considerably from linearity. However the plots of η'' *vs* η' have been found to be linear as reported in Figure 1,2,3 for both the molecules ethyl acetate and n- butyl acetate in P.O. and benzene mixture. It is similar to log τ *vs* log η_s plots as reported earlier [11] for these molecules. The deviation from linearity is interpreted in terms of viscosity losses present at microwave frequencies. The complex viscosity (η^*) and complex shear modulus of rigidity (G^*) observed in ethyl acetate and n-butyl acetate in highly viscous medium of P.O and benzene mixture is consistent with earlier observation [26-28] on polymers. The complex viscosity (η^*) in paraffin oil is due to presence of

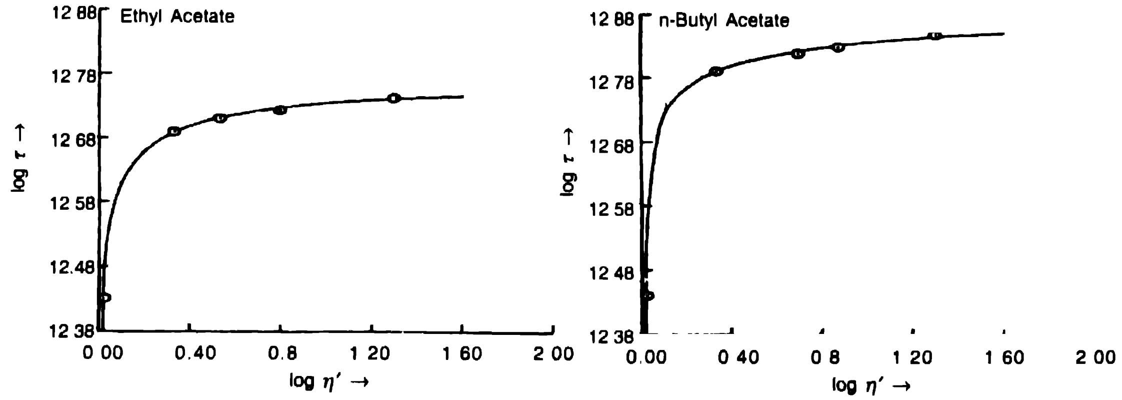

Figure 1. Variation of log τ *vs* log η'.

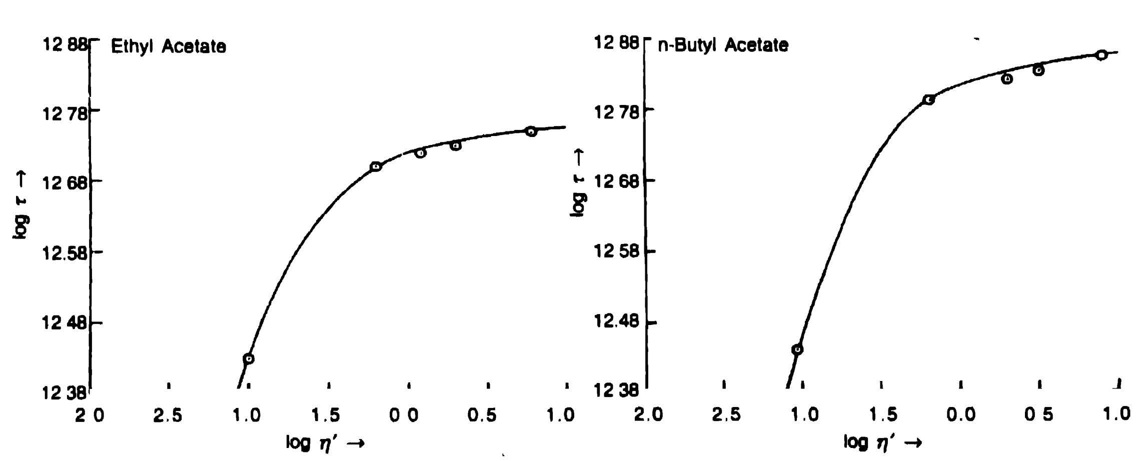

Figure 2. Variation of log τ *vs* log η''.

polymerization of anthracene ring present in paraffin oil [24]. The difference in the viscosity loss is due to damped oscillatory motion of polar molecules in the viscous medium. A hypothetical

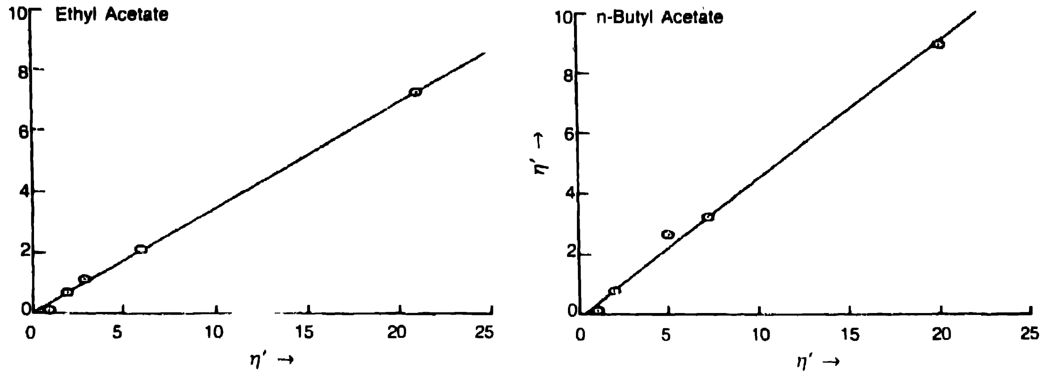

Figure 3. Variation of η'' vs η'

eq (16) has been proposed to represent the viscous losses at microwave frequencies. These results are consistent with our earlier studies on pyridine, quinoline, bromobenzene and iodobenzene at different concentrations of P.O and benzene mixture as solvent [20].

Acknowledgment

The financial assistance by the University Grants Commission New Delhi on minor research project to S.K.S. is gratefully acknowledged.

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